

Persistence of Chlorpyrifos in Soils under Different Moisture Regimes

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Abstract: Chlorpyrifos is an organophosphorus insecticide used to control insect pests in soil. The fate of chlorpyrifos in soils under different moisture regimes is of interest because application directions specify soil-surface treatments for a number of agricultural and urban pests. Chlorpyrifos was degraded rapidly in all air-dry soils and slightly more slowly in soils at field capacity and/or under submerged conditions. Degradation rates were influenced by clay-catalysed hydrolysis under air-dry conditions and neutral or alkaline hydrolysis under submerged conditions. Degradation was faster in Bellary soil (*chromic haplustert*) and slower in Chettalli soil (*ustic palehumult*) under all three moisture regimes. The calculated half-lives ranged from 1.6 to 10.0, 5.2 to 22.0 and 8.7 to 25.1 days under air-dry, field capacity and submergence respectively at an application rate of 10 mg kg⁻¹.

Key words: chlorpyrifos, air-dry, field capacity, submergence, hydrolysis

1 INTRODUCTION

Chlorpyrifos [*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate] is an organophosphorus compound that displays broad-spectrum insecticidal activity against a number of important arthropod pests. It is employed in a wide variety of agricultural and speciality pest-control situations. Examples include its use in corn agriculture in the United States, termite control in Japan, cotton agriculture in Egypt and citrus horticulture in Spain. In India it is recommended mainly for the control of termites and may possibly be a substitute soil insecticide for the phased-out organochlorine insecticides.

In soils, chlorpyrifos may remain biologically active for periods ranging from 20 days to three months.¹ Half-lives determined under laboratory conditions vary greatly and half-life estimates in different soils have ranged from less than 10 days to greater than 120 days.^{2–6} Under field conditions, half-lives for soil-surface applications are typically of the order of a few days to two weeks, whilst soil-incorporated applications have half-lives of one to two months.⁷ Recently Racke *et al.*⁸ examined chlorpyrifos degradation in soils as affected by initial concentration (10, 100 and

1000 µg g⁻¹), soil moisture (field capacity, 1.5 MPa and air-dry) and temperature (15, 25 and 35°C) and noticed significantly retarded degradation at the 1000 µg g⁻¹ compared to the 10 µg g⁻¹ rate of application.

The major environmental factors that influence chlorpyrifos loss in soil are moisture, pH, organic matter and clay content.^{1,5,9} The major routes of chlorpyrifos loss in soil are volatilization, microbial degradation and chemical hydrolysis on dry soil surfaces.^{1,4,5,7,10}

Although chlorpyrifos has not been found to be highly persistent at agricultural application rates (0.56 to 5.6 kg ha⁻¹), its efficacy mainly depends on its application rate and the soil moisture, pH and organic matter content. The purpose of the present study was therefore to determine the dissipation rate of chlorpyrifos in soils under three moisture regimes, namely air-dry, field capacity and submerged conditions.

2 MATERIALS AND METHODS

2.1 Chemical

Analytical-grade chlorpyrifos with a technical purity of 100% supplied by Dow Elanco, Indianapolis, IN 46268 was used in the present study.

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2.2 Soils

Soils used for the study were surface (0–15 cm) samples collected from three benchmark soil series of Karnataka, namely Hesaraghatta (*kandic haplustert*), Chettalli (*ustic palehumult*) and Bellary (*chromic haplustert*). Soils were air-dried, ground and passed through a 2-mm sieve to remove debris, and then stored in plastic containers. The properties of the soils are listed in Table 1.

2.3 Persistence of chlorpyrifos in soil

For chlorpyrifos persistence studies, 20-g portions of soil were placed in 125-ml sample bottles. Chlorpyrifos was added to the soils in 0.5 ml acetone at 10 mg kg^{-1} and mixed thoroughly. Field capacity conditions were maintained by adding the calculated amounts of water and submergence was achieved by adding 30 ml of distilled water so that 1.0 to 1.5 cm of standing water was maintained above the soil. The experimental treatments were replicated three times. The weight of each sample bottle was recorded to permit periodical addition of water to maintain the required moisture regime. The samples were kept at room temperature ($25(\pm 3)^\circ\text{C}$) and the residues were analysed 0, 5, 10, 30, 45 and 60 days after application.

2.4 Extraction and cleanup of chlorpyrifos residues

Chlorpyrifos was extracted from soil with hexane + acetone (9 + 1 by volume; 40 ml). The samples were shaken for one hour on a wrist-action mechanical shaker and then filtered under suction. The filtrate was transferred to a separating funnel. The upper hexane layer was collected and the lower layer was partitioned with further hexane (20 ml), the pooled hexane being dried by passing through a layer of anhydrous sodium sulfate. The extract was then reduced to dryness using a rotary flash evaporator. The sample was redissolved in 10 ml hexane and then transferred to a graduated test tube.

2.5 Analysis of chlorpyrifos residues

The quantitative analysis of chlorpyrifos was done by Gas Liquid Chromatography (GLC) using a Varian GC-3600 equipped with a thermionic specific detector (TSD) and 10% OV-101 stainless steel column (2 m length 3 mm ID). The flow rates of carrier gas (nitrogen), air and hydrogen were 30, 175 and 4.5 ml min^{-1} respectively and the temperatures of column, injector port and detector were 230, 240 and 280°C respectively. Chlorpyrifos had a retention time of 3.20 min under these conditions. Volumes of $1 \mu\text{l}$ were injected and peak area measurements were used to quantify the insecticide residues.

2.6 Recovery analysis

Recovery values were determined by fortification of 20 g soil samples with chlorpyrifos at $10 \mu\text{g g}^{-1}$ soil and replicated three times. Average recoveries of chlorpyrifos from soil under air-dry, field capacity and submerged conditions were 84.8, 88.8 and 90.0% respectively.

2.7 Degradation kinetics

The first-order exponential equation $C = C_0 e^{-kt}$ was used to calculate rate constants, determination coefficients (r^2) and half-lives ($t_{1/2}$) where C is the concentration after time t , C_0 is the initial concentration and k the rate constant. In most cases, the first-order exponential equation provided the best fit to the data ($r^2 > 0.87$).

3 RESULTS AND DISCUSSION

The persistence of chlorpyrifos under the different moisture regimes in the three soils varied considerably (Fig. 1). Degradation of chlorpyrifos was fastest under air-dry conditions irrespective of soil, followed by field capacity and submerged conditions. The chlorpyrifos residues of

TABLE 1
Physico-chemical Properties of the Soils Used

Properties	Hesaraghatta soil	Chettalli soil	Bellary soil
pH (1 : 2.5)	7.09	6.24	9.00
EC (dS m^{-1})	0.19	0.20	0.27
OM (%)	0.9	3.1	4.0
CEC ($\text{meq } 100 \text{ g}^{-1}$)	13.9	17.6	62.4
Clay (%)	20.2	22.5	33.2
Moisture content (%) at field capacity	29.0	38.7	35.6
Taxonomical class (USDA)	Kandic haplustert	Ustic palehumult	Chromic haplustert

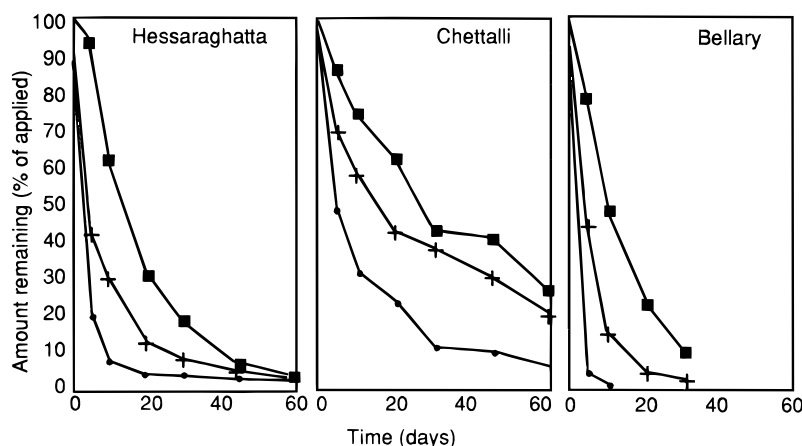


Fig. 1. Persistence of chlorpyrifos in soils under different moisture regimes. ●, Air dry; +, field capacity; ■, submergence.

2.00, 4.79 and 0.37 mg kg⁻¹ in Hesaraghatta, Chettalli and Bellary soils under air-dry conditions on day 5 indicate 80, 62 and 96% degradation of applied chlorpyrifos respectively. The calculated half-lives (Table 2) ranged from 1.6 to 10.0 days under air-dry, 5.2 to 22.0 days at field capacity and 8.7 to 25.1 days under submerged conditions. The faster degradation in air-dry soils may be attributed to a clay-catalysed hydrolysis process and this study supports the hypothesis of Mingelgrin *et al.*¹¹ that clay-catalysed hydrolysis is common for most organophosphorus ester insecticides. It is also closely similar to parathion as reported by Saltzman *et al.*¹² and Mingelgrin and Saltzman¹³ because of the similarities in the molecular structure of the two insecticides. The results of Saltzman *et al.*¹⁴ for parathion and Getzin⁵ for chlorpyrifos further support

the air-dried clay-induced catalysis hypothesis. Saltzman *et al.*¹⁴ found that only a slight increase in moisture content above that of bound water drastically inhibited surface-catalysed hydrolysis of parathion and methyl parathion. Getzin⁵ also made similar observations in mineral soils for chlorpyrifos.

The ability of a soil to catalyse the degradation of chlorpyrifos depends upon a number of factors. These include the quantity of clay, type of clay, organic matter content, moisture content and pH of soil. Saltzman *et al.*¹⁴ showed that the type of clay, incubation temperature, saturating cation and degree of hydration affect the surface-induced hydrolysis rates of organophosphorus esters. The faster degradation of chlorpyrifos in Bellary soil is mainly attributed to high clay content and alkaline pH of the soil which induces the hydrolysis. As reported by Getzin,⁵ the increase in clay content correspondingly increased the quantities of chlorpyrifos hydrolysis products which supports the present findings.

Most insecticides are usually degraded faster in moist soil than in dry soil because moisture encourages microbial activity. Microbial degradation has been shown to be an important route of chlorpyrifos degradation in soil.^{2,15-17} Cleavage and mineralization of the heterocyclic ring of chlorpyrifos occur in soil due to the activities of microorganisms.^{2,7,18,19,24} However Getzin² and Harris and Turnbull²⁰ showed that volatilization of chlorpyrifos is the major dissipation pathway under moist soil conditions. Hence the disappearance of chlorpyrifos under field capacity condition in the present study may be attributed to microbial degradation and volatilization.

Though slower degradation of chlorpyrifos was initially observed in all the soils under the submerged conditions, degradation in both Hesaraghatta and Bellary soils was faster than in the Chettalli soil. This faster degradation may be due to alkaline hydrolysis in the high pH Bellary soil while in Hesaraghatta and Chettalli soils degradation may be due to neutral hydrolysis.¹⁰ It is well known that many organophosphorus

TABLE 2

First-Order Rate Constants (*k*), Determination Coefficients (*r*²) and Half-Lives (*t*_{1/2}) for Chlorpyrifos in Soils under Different Moisture Regimes

	<i>k</i>	<i>r</i> ²	<i>t</i> _{1/2} (days)
<i>Moisture regime</i>	<i>(day⁻¹)</i>		
	Hessaraghatta		
Air-dry ^a	0.252	0.975	2.8
Field capacity ^b	0.079	0.948	8.8
Submergence ^b	0.060	0.984	11.5
	Chettalli		
Air-dry ^c	0.069	0.866	10.0
Field capacity ^b	0.032	0.917	22.0
Submergence ^b	0.028	0.986	25.1
	Bellary		
Air-dry ^a	0.447	0.929	1.6
Field capacity ^b	0.133	0.961	5.2
Submergence ^b	0.080	0.997	8.7

^a Up to 10 days after incubation.

^b Up to 30 days after incubation.

^c Up to 20 days after incubation.

insecticides are hydrolytically unstable at elevated pH and the rates of base-catalysed hydrolysis are often greatly accelerated in moist soil and water at pH values above 7.5.^{10,21-24}

The degradation rate constants, half-lives and determination coefficients in soils are presented in Table 2. The rate constants and half-lives of chlorpyrifos degradation were calculated by considering the persistence data up to 10 or 20 days under air-dry conditions and up to 30 days under submerged conditions and chlorpyrifos degradation was found to follow first-order kinetics with high determined coefficients ($r^2 > 0.87$).

Among the three soils examined here, Chettalli registered slow degradation of chlorpyrifos under all moisture regimes, mainly attributed to high organic matter content, low pH and low clay content. The organic matter had little or no capacity to catalyse hydrolysis of chlorpyrifos and the hydrolysis observed was probably due to its mineral component.

4 CONCLUSIONS

In this study, the major route of chlorpyrifos degradation in soil was found to be clay-catalysed hydrolysis under air-dry condition and microbial degradation, volatilization and hydrolysis are the major routes of degradation under field capacity and submerged conditions.

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